

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : C08G 65/26		A1	(11) International Publication Number: WO 99/05199 (43) International Publication Date: 4 February 1999 (04.02.99)
(21) International Application Number: PCT/EP98/03854 (22) International Filing Date: 24 June 1998 (24.06.98) (30) Priority Data: 97112589.3 23 July 1997 (23.07.97) EP (34) Countries for which the regional or international application was filed: AT et al.		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, GW, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).	
(71) Applicant: IMPERIAL CHEMICAL INDUSTRIES PLC [GB/GB]; Imperial Chemical House, Millbank, London SW1P 3JF (GB). (72) Inventor: GOEGEBEUR, Patrick, Margriet, Gaston; Veldegemstraat 28, B-8210 Zedelgem (BE). (74) Agents: BAKEN, Philippus, Johannes, Leonardus, Henricus et al.; ICI Europe Ltd., ICI Polyurethanes, Intellectual Property Dept., Everslaan 45, B-3078 Everberg (BE).		Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>	
(54) Title: PURIFICATION OF PROPYLENE OXIDE			
(57) Abstract <p>Purification of propylene oxide by distillation shortly before it is used.</p>			

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		

-1-

Purification of propylene oxide

The present invention is concerned with a process for purifying propylene oxide.

Such processes have been widely described.

US 3578568 discloses a method of separating water, methanol, acetone, and 5 acetaldehyde from propylene oxide by extractive distillation using ethylene glycol, propylene glycol, ethylene glycol monomethylether or diethylene glycol monomethylether as the extractive solvent. US 4692535 discloses a process for purifying propylene oxide by contacting the propylene oxide (PO) with an activated carbon or attapulgite adsorbent. The amount of poly (propylene oxide) is reduced. In comparative tests it is indicated that 10 distilled propylene oxide containing poly (propylene oxide) leads to foam collapse and that distilled propylene oxide which has been heated to 82°C in a carbon steel container for 2 and 7 days also leads to foam collapse; the specification neither discloses how these propylene oxides were distilled nor that distilled propylene oxide could be used; it actually discloses that the way to prevent foam collapse is to use propylene oxide which has been 15 treated with the aforementioned adsorbent.

US 3580819 discloses a process for recovering propylene oxide from a crude propylene oxide comprising propylene, water and higher boiling oxygen-containing impurities by subjecting it to a two-stage distillation process followed by contacting with a liquid aqueous selective solvent for propylene oxide (PO) and distilling PO from the solvent. 20 The starting material has a PO content of 8.1% w only. FR 1469339 and US 3398062 discloses the purification of crude propylene oxide comprising propylene chloride, water, dissolved gas, acetaldehyde and propionaldehyde by distillation and leading the top stream through a separator. The starting material contains a relatively low amount of propylene oxide (88%) and the distillation is conducted at relatively extreme conditions 25 using steam. GB 1040783 discloses a process for making polyethers wherein the PO is introduced trough a reflux column into a reaction vessel. Most of the PO in the reaction vessel evaporates and is returned to the reflux column where it is condensed and the liquid mixture at the bottom of the reflux column is fed back into the reaction vessel. Apart from removal of inert gas no purification of PO takes place. US 5160587 and US 30 5133839 are other examples of disclosures of extractive distillation of PO. In 5160587 a comparative distillation without extractive distillation solvent is shown; the distillation column has a rather high number of plates and the amount of impurities in the PO which is used as starting material is still rather high. Despite the sophisticated purification

-2-

improvement. It was found that over time the quality of the propylene oxide deteriorates which is reflected in the quality of the polyether polyols prepared therefrom and in the quality of polyurethanes made of such polyols. It seems that storage or transport of the PO at ambient temperature could have a negative effect; such storage or transport preferably 5 should take place at a temperature as low as possible but above the melting point of PO. Further it seems that storage or transport of the PO while in contact with mild steel or carbon steel could have a negative effect especially when such steel has been allowed to be in contact with air, moisture, water or oxygen; such storage or transport preferably should take place while the PO is in contact with stainless steel or steel coated with an 10 inert layer. Since variable ways of storage and transport are being used by PO producers, users are faced with commercial grades of PO of variable quality, such quality ultimately effecting the quality of products made therefrom. To date it is not fully understood which change in the propylene oxide causes the deterioration of the polyol and polyurethane quality. In view of the above, there is a need for a PO having a good 15 and consistent quality for use in making materials, in particular polyether polyols and there is a need for a simple process to achieve this.

Surprisingly it was found that, despite the fact that the cause is not fully known, the quality of polyols and polyurethanes could be greatly improved if the propylene oxide is subjected to a simple distillation shortly before it is consumed to make the polyols. 20 Further it was surprisingly found that the quality of PO, which already has a high degree of purity, can be improved by a simple distillation process.

Therefore the invention is concerned with a process for purifying propylene oxide by distillation characterized in that the distillation is conducted shortly before the propylene oxide will be used and with the use of PO which PO has been subjected to distillation 25 shortly before its use and to a process for preparing a material from PO wherein the PO has been subjected to distillation shortly before its use. Further the invention is concerned with a process for purifying PO by distillation wherein the PO starting material preferably has less than 0.2% by weight, more preferably less than 0.1% weight and most preferably less than 0.05% by weight of impurities and wherein 1-10 actual trays are 30 used.

The distillation preferably is carried out less than 1 week before the PO is used, more preferably less than 4 days before it is used and most preferably less than 2 days before

it is used. The PO may be used immediately after the distillation.

The PO used for the distillation may be any PO containing low amounts of impurities, in particular any commercially available PO may be used. Preferably the PO comprises less than 0.2% by weight, more preferably less than 0.1% weight and most preferably 5 less than 0.05% by weight of impurities.

The distillation may be conducted by simply evaporating the PO and collecting the evaporated PO and preferably is conducted in a conventional distillation column supplied with a heater at the bottom or mounted with a heating jacket and coil and a condenser at or near the top of the column together with a vent for releasing inert gas which is supplied 10 together with the PO. In order to avoid entrainment of droplets in the vapour stream the column may contain 1-10 actual trays and preferably 2-8 actual trays. The PO is supplied from a main storage tank for PO under an inert gas blanket at the bottom of the distillation column, heated and allowed to condens in the condensor. From the condensor it is stored as a liquid in an intermediate storage tank until the purified PO is 15 used for making a material or it is fed directly into the process using it. The inert gas preferably is N₂. The distillation process may be conducted at atmospheric pressure or slightly increased pressure (1-3 bar abs) and at 35-60°C or at a pressure of 0.99 to 0.5 bar abs and ambient temperature (a heater is not needed then). The first alternative is preferred. The distillation process may be conducted batchwise, semi-continuously and, 20 preferably, continuously. No chemicals other than the inert gas are added to the PO.

The devices used for the storage and distillation are preferably designed in such a way that all contact of PO with metal surfaces are with stainless steel surfaces. The condensor may be supplied with water at ambient temperature as the means to cool. Preferably, no additional purification of the PO takes place between the distillation 25 according to the present invention and the use of the thus purified PO.

At the bottom of the distillation column impurities will accumulate. This bottom fraction may be removed continuously or discontinuously. The bottom fraction may be incinerated, purified separately, fed back to the main storage tank or used for applications wherein the presence of such impurities have no or less effect, like for the making of 30 glycols and glycol ethers and for making polyols used for making rigid polyurethane foams.

The purified PO may be used for any application for PO known, especially for the preparation of polymers and more in particular for polyether polyols, especially those having an equivalent weight of 500 or more, preferably of 1000 or more and containing at

least 10% by weight, preferably at least 25% by weight and most preferably at least 50% by weight of oxypropylene units.

Such polyether polyols are known in the art as well as the processes to make them. The PO is fed as a liquid from the intermediate storage tank or the condenser of the 5 distillation column to the reactor to make the polyether polyols. They may be homopolymers of PO and copolymers of PO with other alkylene oxides, like ethylene oxide and butylene oxides. The copolymers may be block copolymers, random copolymers or combinations thereof. The present invention is also concerned with such materials, especially such polyether polyols made from PO purified according to the 10 present invention.

Such polyether polyols may be used in the preparation of polyurethanes, in particular polyurethane foams, especially flexible foams and elastomers. The present invention is further related to such polyurethanes.

The present invention is illustrated by the following examples.

15 Example 1

a) Commercial propylene oxide which was transported via a carbon steel pipeline of about 300 meters and which had an amount of impurities of less than 0.2% by weight was used. Half the amount of this PO was distilled at 50°C and atmospheric pressure, condensed and collected (using N₂ as inert gas and a reactor with 1 actual tray mounted 20 with a jacket and coil, a condenser near the top and venting means at the top).

b) The undistilled PO was added to an equal amount of polyol (Arcol 1374, a polyol widely used for preparing flexible polyurethane foams, sold by Arco). Next the PO was removed from the polyol by vacuum distillation until less than 50 parts per million (ppm) of PO is left in the polyol.

25 c) Step b) was repeated with fresh Arcol 1374 and PO distilled in step a), which was used within 1 day after distillation.

Flexible foams were made in identical ways using Arcol 1374 treated with undistilled PO (code TAU) and Arcol 1374 treated with distilled PO (code TAD).

110 parts by weight of the following polyol composition was reacted with 75 parts by 30 weight of Suprasec 2420, which is an MDI-based polyisocyanate prepolymer obtainable

from Imperial Chemical Industries PLC (Suprasec is a trademark of ICI). Step 1 b), 1 c) and the flexible foam preparation were conducted within 3 days after distillation of the PO in step a).

Polyol composition (in parts by weight) :

TAU	90	-
TAD	-	90
Daltocel F 417 ¹⁾	10	10
water	3.8	3.8
diethanolamine	0.1	0.1
diethyltoluene diamine	0.6	0.6
Dabco™ R8020, catalyst ²⁾	0.3	0.3
Dabco 8154, catalyst ²⁾	0.4	0.4
Niax™ A1, catalyst ²⁾	0.1	0.1
Tegostab™ B4113, surfactant ²⁾	0.5	0.5

5 ¹⁾ polyol from ICI, Daltocel is a trademark of ICI

²⁾ commercially available

The ingredients were poured, mixed and allowed to react in an open container. The height/weight ratio (H/W) of the foams was determined.

The results are as follows :

	H/W	Structure
TAU	147	very coarse cell structure
TAD	182	nice cell structure

10 Example 2

Propylene oxide which was shipped in a stainless steel cylinder and which had a level of impurities of less than 0.2% by weight was used.

PO was charged to a 12 liter stainless steel reactor, which was 3 times flushed with N₂ to remove all air. The distillation outlet of the reactor was opened (the reactor did not contain a fractionation column; hence the number of actual trays was one) and the PO was heated from ambient temperature to 40-45°C and kept at that temperature for 5 hours (the reactor was mounted with a heating jacket with a coil; water was used as the heating fluid in the coil). A small nitrogen bleed was applied at the end of the distillation. The PO was collected at the bottom of the condenser in a glass flask. The amount of

-6-

distilled PO collected was about 14.9 kg (the distillation was conducted in 2 batches).

Examples 1 b and 1 c were repeated using undistilled PO from the above cylinder and distilled PO made as described above and which had been stored for 2 days in said glass flasks. Flexible foams were made as described in example 1. The H/W ratio for TAD 5 was 18% higher than the ratio for TAU.

Example 3

In this example undistilled and distilled PO (after 2 days storage in the glass flask) from example 2 was used.

In a standard way a glycerol initiated polyoxypropylene polyol having an OH value of 352 10 mg KOH/g was propoxylated and ethoxylated to give a polyol with an OH value of 28 mg KOH/g and with 15.4% by weight oxyethylene groups (all tipped).

The propylation of part of the polyol with OH value of 352 mg KOH/g was conducted with undistilled PO while the propylation of the other part was conducted with distilled PO.

15 From the polyols so obtained foams were made as in example 1.

The flexible polyurethane foam wherein undistilled PO was used had a coarse cell structure, a recession of 11.4% and a H/W ratio of 176 while the foam wherein distilled PO was used had a nice, fine cell structure, a H/W ratio of 188 and a recession of 7%. (all measurements conducted 24 hours after the foam was made).

CLAIMS

1. Process for purifying propylene oxide by distillation characterized in that the distillation is conducted shortly before the propylene oxide will be used.
2. Process according to claim 1 wherein the distillation takes place less than 1 week 5 before its use.
3. Process according to claims 1-2 wherein the distillation takes place less than 4 days before the propylene oxide will be used.
4. Process according to claims 1-3 wherein the distillation takes place less than 2 days before the propylene oxide will be used.
- 10 5. Process according to claims 1-4 wherein the distillation is conducted at 1-3 bar abs and 35-60°C.
6. Process according to claims 1-4 wherein the distillation is conducted at ambient temperature and 0.99 to 0.5 bar abs.
7. Process according to claims 1-6 wherein the propylene oxide before distillation 15 contains less than 0.2% by weight of impurities.
8. Process according to claims 1-7 wherein the propylene oxide before distillation contains less than 0.1% by weight of impurities.
9. Process according to claims 1-8 wherein the propylene oxide before distillation contains less than 0.05% by weight of impurities.
- 20 10. Process according to claims 1-9 wherein 1-10 actual trays are used.
11. Process according to claims 1-10 wherein 2-8 actual trays are used.
12. Process according to claims 1-11 wherein no chemicals other than an inert gas are added to the PO.

13. Process for purifying propylene oxide by distillation characterized in that the propylene oxide before distillation contains less than 0.2% by weight of impurities and that 1-10 actual trays are used.

14. Process according to claim 13 wherein the distillation is conducted at 1-3 bar 5 abs and 35-60°C.

15. Process according to claim 13 wherein the distillation is conducted at ambient temperature and 0.99 - 0.5 bar abs.

16. Process according to claims 13- 15 wherein the propylene oxide before distillation contains less than 0.1% by weight of impurities.

10 17. Process according to claims 13-16 wherein the propylene oxide before distillation contains less than 0.05% weight of impurities.

18. Process according to claims 13-17 wherein 2-8 actual trays are used.

19. Process according to claims 13-18 wherein no chemicals other than an inert gas are added to the PO.

15 20. The use of a propylene oxide made according to claims 1-19.

21. The use according to claim 21 wherein the use is the making of a polymer.

22. The use according to claims 20-21 wherein the use is the making of a polyether polyol.

23. The use according to claims 20-22 wherein the use is the making of a polyether polyol having an equivalent weight of 500 or more and an oxypropylene content of at least 10% by weight.

24. Polymer made using propylene oxide purified according to claims 1-19.

25. Polymer according to claim 24 wherein the polymer is a polyether polyol.

-9-

26. Polymer according to claims 24-25 wherein the polymer is a polyether polyol having an equivalent weight of 500 or more and an oxypropylene content of at least 10% by weight.

27. Polyurethane made from a polymer according to claims 24-26.

5 28. Polyurethane according to claim 27 wherein the polyurethane is an elastomer or a flexible foam.

INTERNATIONAL SEARCH REPORT

Interna	Application No
PCT/EP 98/03854	

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08G65/26

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C08G C07D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 692 535 A (LARSON HAROLD V ET AL) 8 September 1987 cited in the application see table 1 see column 3, line 35 - line 65 ---	1-4, 20-28
X	US 5 160 587 A (MARQUIS EDWARD T ET AL) 3 November 1992 cited in the application see claim 1 see column 1, line 1 - line 20 ---	1,5-20
A	US 3 578 568 A (WASHALL THOMAS A) 11 May 1971 cited in the application see claim 1 see column 3, line 45 - column 4, line 20 ---	1-20 -/-

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

Date of mailing of the International search report

9 November 1998

25/11/1998

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl.
Fax: (+31-70) 340-3018

Authorized officer

O'Sullivan, T

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 98/03854

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 3 881 996 A (SCHMIDT JOHN P) 6 May 1975 cited in the application see claim 1; example 1 -----	1-20
A	GB 1 040 783 A (FARBENFABRIKEN BAYER AKTIENGESELLSCHAFT) 1 September 1966 cited in the application see example 1 -----	1-28

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 98/03854

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
US 4692535	A 08-09-1987	EP 0275680 A JP 2561096 B JP 63166873 A KR 9508280 B		27-07-1988 04-12-1996 11-07-1988 27-07-1995
US 5160587	A 03-11-1992	CA 2070878 A DE 69201047 D DE 69201047 T EP 0540224 A JP 5194456 A		02-05-1993 09-02-1995 11-05-1995 05-05-1993 03-08-1993
US 3578568	A 11-05-1971	BE 741763 A DE 1954520 A FR 2024951 A GB 1216649 A NL 6917421 A, B		19-05-1970 11-06-1970 04-09-1970 23-12-1970 02-06-1970
US 3881996	A 06-05-1975	BE 822375 A DE 2454115 A FR 2251561 A GB 1420058 A JP 50083305 A NL 7414964 A, B		20-05-1975 22-05-1975 13-06-1975 07-01-1976 05-07-1975 23-05-1975
GB 1040783	A	NONE		